

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
25 January 2001 (25.01.2001)

PCT

(10) International Publication Number
WO 01/06578 A2

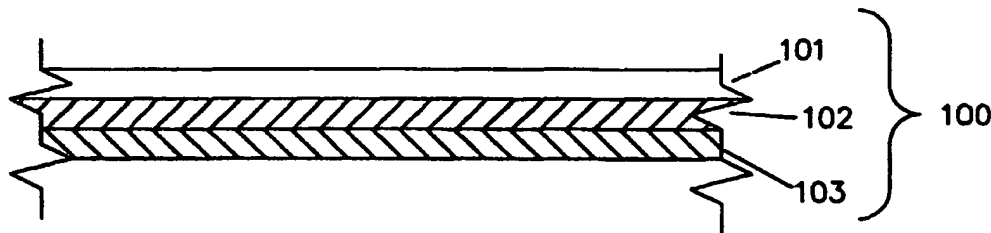
- (51) International Patent Classification⁷: H01M (74) Agent: FREILICH, Arthur; P.O. Box 905, Santa Clarita, CA 91380-9005 (US).
- (21) International Application Number: PCT/US00/19348 (81) Designated States (*national*): AE, AL, AU, BA, BB, BG, BR, CA, CN, CR, CU, CZ, DM, EE, GD, GE, HR, HU, ID, IL, IN, IS, JP, KP, KR, LC, LK, LR, LS, LT, LV, MA, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, US, UZ, VN, YU, ZA.
- (22) International Filing Date: 14 July 2000 (14.07.2000)
- (25) Filing Language: English
- (26) Publication Language: English (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- (30) Priority Data:
60/144,146 16 July 1999 (16.07.1999) US
- (71) Applicant (*for all designated States except US*): QUAL-LION, LLC [US/US]; P.O. Box 905, Santa Clarita, CA 91380-9005 (US).
- (72) Inventors (*for US only*): HISASHI, Tsukamoto; 28445 Via Joyce Drive, Saugus, CA 91350 (US). CHANANIT, Sintuu; 15319 Brook Arbor Court, Houston, TX 77062 (US).

Published:

— Without international search report and to be republished upon receipt of that report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: LITHIUM THIN FILM LAMINATION TECHNOLOGY ON ELECTRODE TO INCREASE BATTERY CAPACITY



WO 01/06578 A2

(57) Abstract: Lithium is laminated onto or into an electrode structure comprising a metal conducting layer with an active material mixture of, for example, a nano-composite of silicon monoxide, together with graphite and a binder, such as polyvinyl di-fluoride (PVDF). The lamination of lithium metal onto or into the electrode structure will reduce the amount of irreversible capacity by readily supplying a sufficient amount of lithium ions to form the initial solid electrolyte interface. In order to laminate lithium metal onto or into the negative electrode, the lithium is first deposited onto a carrier, which is then used to laminate the lithium metal onto or into the electrode structure. The next step is placing the coated electrode material and the lithium-deposited plastic between two rollers or two plates. The rollers or plates are heated to about 120° C or within the range of 25° C to 250° C. A pressure of 50 kg/cm² to 600 kg/cm² is applied to the rollers. The speed of movement of the materials through the roller pair or the plate pair is in the range of 10 cm/min to 5 m/min. The method can be used for either single-sided or double-sided coating. Using this technology alone, the battery capacity can increase by 7% to 15%.

5 LITHIUM THIN FILM LAMINATION TECHNOLOGY ON ELECTRODE
 TO
 INCREASE BATTERY CAPACITY

10 FIELD OF THE INVENTION

This invention relates to a method and apparatus for reducing the irreversible capacity of a rechargeable battery, in particular lithium ion batteries, in order to increase the battery's overall energy storage capacity.

15 BACKGROUND OF THE INVENTION

Batteries typically exhibit irreversible capacities after the initial cycle of charging. The significant capacity lost in the first cycle results in a loss in overall battery storage capacity. The irreversible capacity is due to the formation of the solid electrolyte interface (SEI) layer in typical negative
20 electrodes from the first cycle of charging. However, other forms of irreversible capacity may be due to additional reasons, for example, cavities in the active material of the electrode structure may need to be initially filled with lithium ions before lithium ion insertion can proceed.

SUMMARY OF THE INVENTION

25 The present invention is directed to a method and apparatus for reducing the irreversible capacity of a lithium ion battery by initially depositing a layer of lithium metal onto or into the electrode structure. The deposited lithium serves to form the initial SEI layer before cycling to thus reduce the amount of irreversible capacity and increase the overall battery

5 storage capacity.

A typical electrode structure is comprised of a conducting metal substrate coated with an active material mixture. For example, a typical negative electrode consists of a copper substrate coated with a mixture of graphite and a binder such as polyvinyl di-fluoride (PVDF). In accordance
10 with the present invention, a lithium layer is deposited onto or into the electrode active material to reduce the amount of irreversible capacity by filling voids in the active material that do not participate in the reversible lithium ion insertion process.

In accordance with a preferred embodiment, lithium metal is first
15 deposited onto a carrier, which is then used to transfer the lithium metal to the electrode structure by the application of heat, vacuum, and/or pressure. The carrier preferably comprises a long strip of plastic substrate that is preferable for a continuous transfer of lithium onto or into the electrode. In addition, this approach lends itself to commercial
20 production. The substrate could be one of several materials such as ortho-polypropylene (OPP), Polyethylene Terephthalate (PET), polyimide, or other type of plastic. Lithium metal can be deposited onto or into one or both surfaces of the substrate. The lithium-coated plastic and the electrode material are then placed between two rollers or two
25 plates. Lithium is transferred onto or into the electrode active material by applying heat and/or pressure in vacuum. The rollers or plates are

5 heated in vacuum to about 120°C, or within the range of 25°C to 350°C.
A pressure of 50 kg/cm² to 600 kg/cm² is applied to the rollers. Similarly,
in the case of two plates, a pressure of 50 kg/cm² to 600 kg/cm² is
applied to the sheets of material between them.

The speed of movement of the carrier electrode material through the
10 roller pair or the plate pair is in the range of 10 cm/min. to 5 m/min. For a
given speed, the length of time the materials are exposed to the heat and
pressure rollers, or alternatively the heat and pressure plates, will be
fixed, depending only on the lengthwise distance of the plate along the
direction of the material movement. For the roller pair, deformation of the
15 rollers results in distance in the direction of travel of the material, which
adds to the actual contact time of pressure and temperature application.
The method could be used for either single-sided coating or double-sided
coating. In the double-sided coating method, both sides of the metal
substrate are coated with active material. The coated metal substrate is
20 then sandwiched between two lithium-coated plastic carriers, with the
lithium sides facing the active material on the coated metal substrate. All
three sheets are then fed into a mechanism for applying heat and/or
pressure in vacuum. As a result, lithium is transferred to both sides of
the electrode structure, i.e., the coated metal substrate.

25 The thickness of lithium transferred onto the electrode structure can be
controlled to produce a lithium coating between about 50 Angstroms and

5 0.3 millimeters. Using this technology, it is expected to increase a lithium
ion battery capacity by about 7% to 15%.

BRIEF DESCRIPTION OF THE DRAWINGS

The above and other features and advantages of the invention will
be more apparent from the following detailed description wherein:

10 Figure 1 shows the electrode structure coated with active material;

Figure 2 shows the structure of the film of lithium metal deposited
on the plastic substrate;

Figure 3A shows the roller pair system that will be used to transfer
the lithium from the carrier to the electrode by applying heat and pressure
15 in vacuum;

Figure 3B shows the plate pair system that will be used to transfer
the lithium from the carrier to the electrode by applying heat and/or
pressure in a vacuum atmosphere;

Figure 4 shows the first cycle of an example negative electrode, a
20 SiO nano-composite electrode that has not been laminated with lithium.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following text describes the preferred mode presently
contemplated for carrying out the invention and is not intended to
25 describe all possible modifications and variations consistent with the
spirit and purpose of the invention. This description is not to be taken in

5 a limiting sense, but is merely made for the purpose of describing the general principles and preferred manner of practicing the invention. The scope of the invention should be determined with reference to the claims.

The objective of this invention is to significantly reduce the irreversible capacity produced mainly from the first cycle life of the active material of an electrode. A reduction in the irreversible capacity will ultimately lead to an overall increase in battery capacity. Lithium is transferred to the electrode by lamination of lithium metal onto or into an electrode structure. This electrode structure has a metal conducting layer coated with an active material. For example, negative active material is typically a mixture of graphite and PVDF. The lamination of lithium metal onto or into the electrode structure will reduce the amount of irreversible capacity by readily supplying sufficient lithium to fill any voids in the active material, which do not participate in the reversible lithium insertion process.

Figure 1 shows the structure of an electrode (100), having a lithium coating (101) in accordance with the present invention. The substrate (103) for negative electrodes is usually copper foil but other types of material such as a copper-plated polymer may be used.

25 However, it must be noted that the substrate should not react with lithium metal, which is why copper is most often used as the negative electrode

5 substrate. The metal of the electrode may be coated with, for example, a mixture of graphite and silicon oxide (102). A suitable mixture of about 20% SiO nano-composite and 80% graphite for a negative electrode has an ability to create a capacity of about 500 mAh/g as compared to graphite's theoretical capacity of 372 mAh/g. This results in a significant
10 increase in the rechargeable capacity. However, such a mixture also has significant irreversible capacity, making the present invention greatly beneficial for such an electrode.

In order to laminate lithium metal (Figure 2, 201) to the electrode (100), the lithium (201) is deposited onto a carrier (202), which is then
15 used to apply the lithium metal to the electrode structure. The carrier preferably comprises a long strip of plastic substrate.

Figure 3A details the process in which lithium will be transferred from the carrier substrate to the electrode. The left side of the figure is prior to lithium printing, while the right side is after lithium printing. The
20 preferred embodiment consists of two rollers (305) or plates (Figure 3B, 306) with lithium plus carrier substrate (301) placed between the two rollers or plates. In addition, pressure will be applied to the rollers (Figure 3A, 305), or plates (Figure 3B, 306) and as the electrode (303) and lithium-deposited carrier substrate (301) move through the rollers
25 (304), or plates, the lithium metal (201) will be laminated onto or into the electrode (100).

5 Figure 4 is a graph of the first cycle of a SiO nano-composite cell that has not been initially laminated with lithium metal. If the discharge curve is transposed along an imaginary axis, it is clear that there is a large initial irreversible capacity that must be reduced in order to increase battery capacity.

10 While the invention herein disclosed has been described by means of specific embodiments and applications thereof, numerous modifications and various could be made thereto by those skilled in the art without departing from the scope of the invention set forth in the claims.

15

20

25

5

CLAIMS

10 What is claimed is:

1. A method to laminate lithium onto an electrode comprising the steps of:

- (a) utilizing an electrode structure coated with active material consisting of, as a negative electrode example, a mixture of
15 graphite and a binder;
 - (b) utilizing lithium coated plastic sheet where in said plastic sheet is selected from the group consisting of oriented polypropylene (OPP) polyethylene Terephthalate, and polyimide;
 - (c) pressing the said electrode material and said lithium coated
20 material together using a pair of pressing structures;
 - (d) applying pressure and heat in vacuum to said materials while they are pressed together by said pressing structures;
 - (e) moving said materials through the pressing structures
25 while applying continuous pressure and heat to said materials as they move through said pressing structures.
2. The method of claim 1 further comprising the step of utilizing the said laminated electrode in lithium or lithium ion batteries.
 3. The method of claim 1 further comprising the step of utilizing a pair
30 of rollers as the pressing structures.
 4. The method of claim 1 further comprising the step of utilizing a pair of plates as the pressing structures.

- 5 5. The method of claim 1 further comprising the step of applying heat
in a vacuum atmosphere by utilizing said pressing structures at a
temperature within the range 25°C to 250°C.
6. The method of claim 1 further comprising the step of applying
pressure in the range of 50 kg/cm² to 600 kg/cm² utilizing said
10 pressure structures.
7. A method for increasing the storage capacity of a lithium ion battery
including the steps of:
- (a) providing an electrode structure comprised of a metal
 substrate coated with active material; and
- 15 (b) depositing lithium onto or into said active material to
 reduce cavities therein.
8. The method of claim 7 wherein said depositing step includes:
- (a) providing a sheet carrier bearing a layer of lithium metal;
 and
- 20 (b) pressing said layer of lithium metal against said active
 material to transfer lithium onto or into said active material.
9. The method of claim 8 wherein said depositing step further includes:
- (a) applying heat and/or pressure in vacuum to said carrier
 and/or said electrode structure to facilitate transfer of said
25 lithium.

30

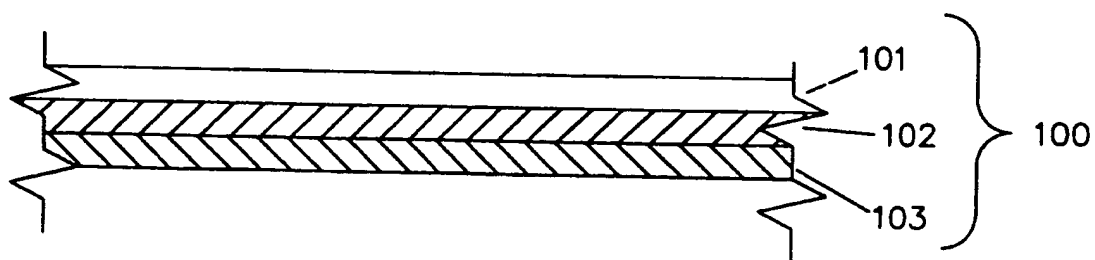


Fig 1

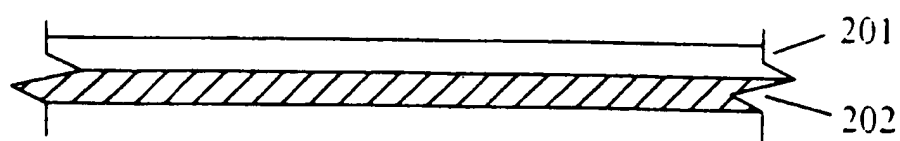
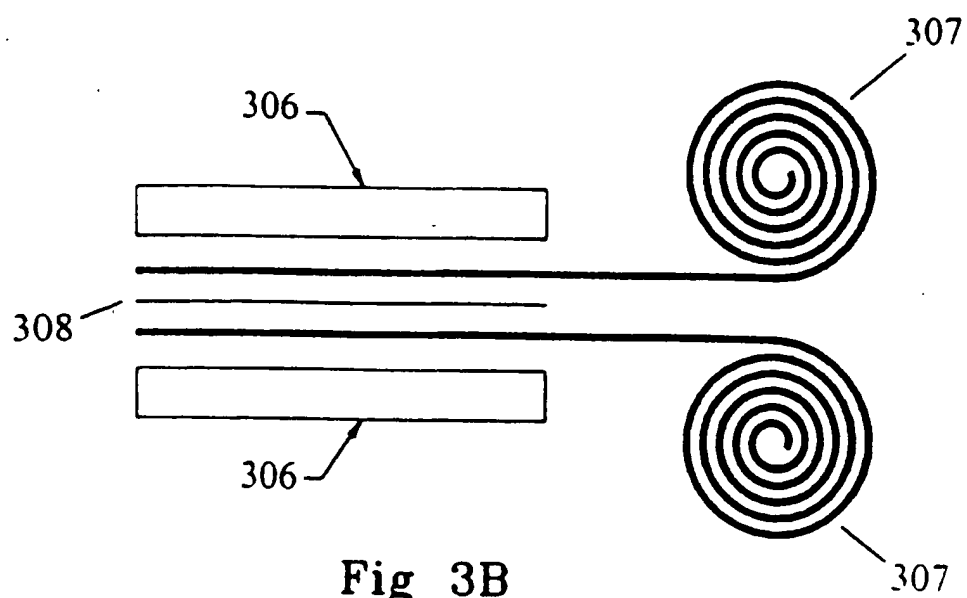


Fig 2

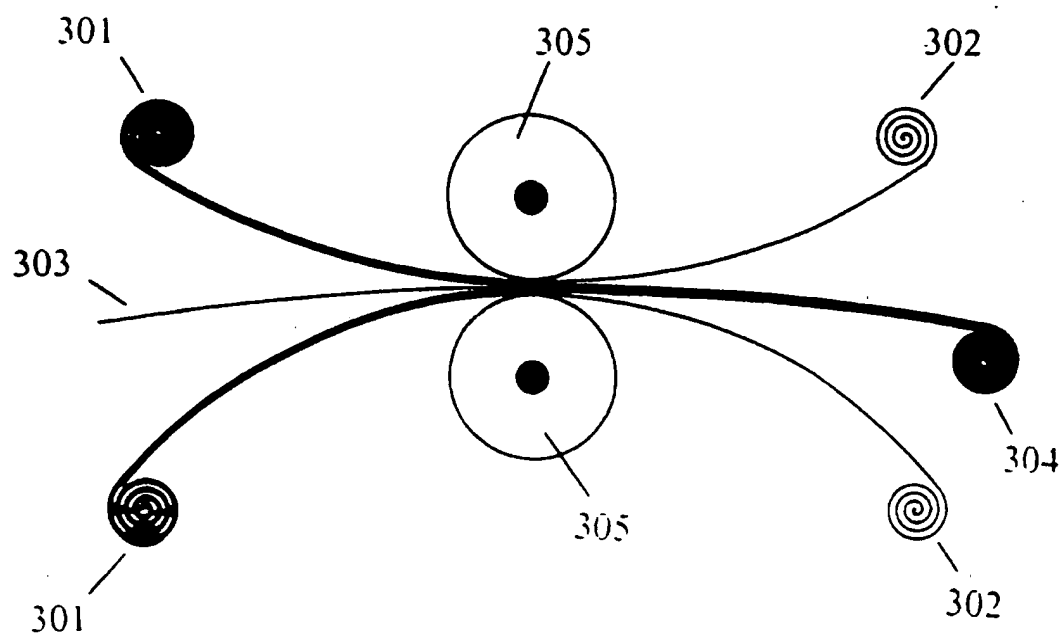


Fig 3A

Large irreversible capacity of first cycle of SiO nano-composite cell

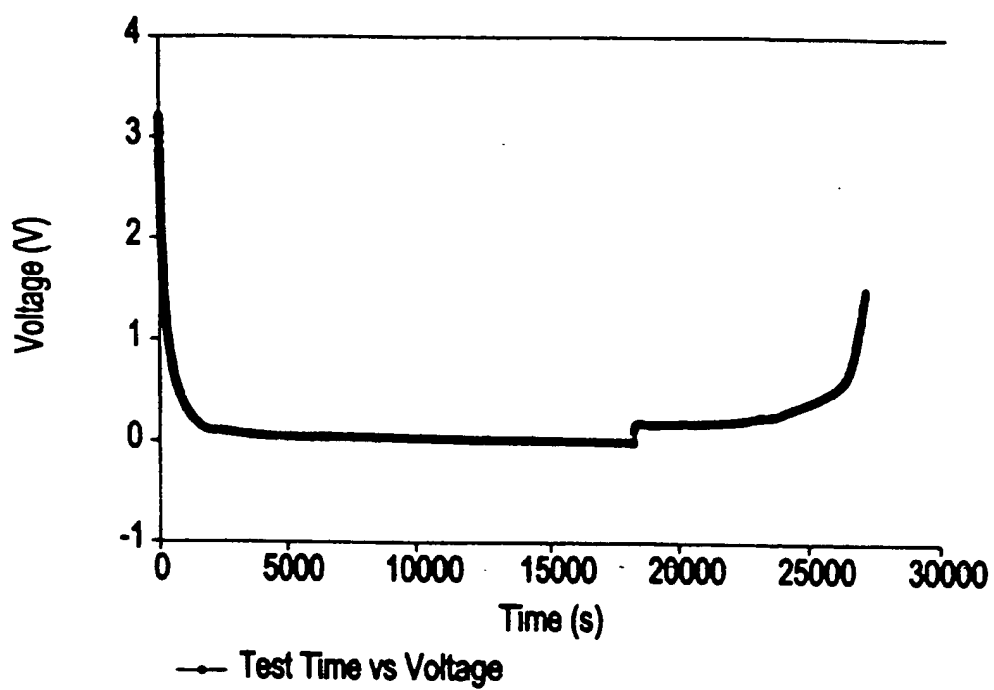


Fig 4

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



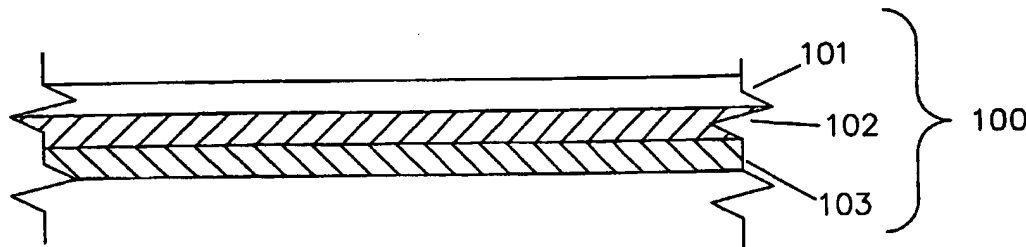
(43) International Publication Date
25 January 2001 (25.01.2001)

PCT

(10) International Publication Number
WO 01/06578 A3

- (51) International Patent Classification⁷: H01M 10/40, 4/02, 4/04
- (21) International Application Number: PCT/US00/19348
- (22) International Filing Date: 14 July 2000 (14.07.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/144,146 16 July 1999 (16.07.1999) US
- (71) Applicant (for all designated States except US): QUAL-
LION, LLC [US/US]; P.O. Box 905, Santa Clarita, CA
91380-9005 (US).
- (72) Inventors (for US only): HISASHI, Tsukamoto; 28445
Via Joyce Drive, Saugus, CA 91350 (US). CHANANIT,
Sintuu; 15319 Brook Arbor Court, Houston, TX 77062
(US).
- (74) Agent: FREILICH, Arthur; P.O. Box 905, Santa Clarita,
CA 91380-9005 (US).
- (81) Designated States (national): AE, AL, AU, BA, BB, BG,
BR, CA, CN, CR, CU, CZ, DM, EE, GD, GE, HR, HU, ID,
IL, IN, IS, JP, KP, KR, LC, LK, LR, LS, LT, LV, MA, MG,
MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA,
US, UZ, VN, YU, ZA.
- (84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG,
CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report
- (88) Date of publication of the international search report:
11 October 2001

(54) Title: LITHIUM THIN FILM LAMINATION TECHNOLOGY ON ELECTRODE TO INCREASE BATTERY CAPACITY



(57) Abstract: Lithium is laminated onto or into an electrode structure comprising a metal conducting layer with an active material mixture of, for example, a nano-composite of silicon monoxide, together with graphite and a binder, such as polyvinyl di-fluoride (PVDF). The lamination of lithium metal onto or into the electrode structure will reduce the amount of irreversible capacity by readily supplying a sufficient amount of lithium ions to form the initial solid electrolyte interface. In order to laminate lithium metal onto or into the negative electrode, the lithium is first deposited onto a carrier, which is then used to laminate the lithium metal onto or into the electrode structure. The next step is placing the coated electrode material and the lithium-deposited plastic between two rollers or two plates. The rollers or plates are heated to about 120° C or within the range of 25° C to 250° C. A pressure of 50 kg/cm² to 600 kg/cm² is applied to the rollers. The speed of movement of the materials through the roller pair or the plate pair is in the range of 10 cm/min to 5 m/min. The method can be used for either single-sided or double-sided coating. Using this technology alone, the battery capacity can increase by 7% to 15%.

WO 01/06578 A3

INTERNATIONAL SEARCH REPORT

Inter. Appl. No.

PCT/US 00/19348

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01M10/40 H01M4/02 H01M4/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 02, 26 February 1999 (1999-02-26) -& JP 10 302839 A (JAPAN STORAGE BATTERY CO LTD), 13 November 1998 (1998-11-13) abstract	1-4
A	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 09, 30 July 1999 (1999-07-30) -& JP 11 111267 A (TOYOTA MOTOR CORP), 23 April 1999 (1999-04-23) abstract	1,7
	--- -/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

2 May 2001

Date of mailing of the international search report

09/05/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Riba Vilanova, M

INTERNATIONAL SEARCH REPORT

Interr. nel Application No

PCT/US 00/19348

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 27908 A (UNIV RAMOT ; SHOSHAN HERBERT Z (IL); PELED EMANUEL (IL); MENACHEM C) 12 September 1996 (1996-09-12) page 1, line 3 - page 2, line 21 page 4, line 5 - line 20 -----	1,7
A	DE 198 39 244 A (SAMSUNG DISPLAY DEVICES CO LTD) 18 March 1999 (1999-03-18) page 1, line 19 - line 58 -----	1,7
A	CA 2 203 490 A (HYDRO QUEBEC) 23 October 1998 (1998-10-23) the whole document -----	1-6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/19348

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 10302839 A	13-11-1998	NONE	
JP 11111267 A	23-04-1999	NONE	
WO 9627908 A	12-09-1996	AU 5304696 A	23-09-1996
DE 19839244 A	18-03-1999	GB 2328786 A	03-03-1999
		JP 11126633 A	11-05-1999
CA 2203490 A	23-10-1998	CA 2235884 A	23-10-1998
		EP 0875952 A	04-11-1998
		JP 11097065 A	09-04-1999
		US 6030421 A	29-02-2000